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Analytical Methods

Paper

A novel method for quantification of Decabromodiphenyl ether in plastics without sample preparation using Direct Insertion Probe – Magnetic Sector High Resolution Mass Spectrometry.

A. Guzzonato[a], H. Mehlmann[b], D. Krumwiede[b], S.Harrad[a].

We report a rapid, efficient analytical method for detecting Brominated Flame Retardants (BFRs) in plastic materials using Direct Insertion Probe with double focusing magnetic sector high resolution mass spectrometry. We acquired the total ion spectrum (30 to 1000 m/z) and observed 959 and 799 m/z ions respectively for quantification and evaluation of the fragmentation reproducibility of decabromodiphenyl ether (BDE209, MW 959 amu). *Ad-hoc* prepared Acrylonitrile Butadiene Styrene (ABS) solid reference materials (RMs) containing different concentrations of BDE209 were used to develop a 5-point calibration curve that showed linearity (R^2> 0.999) over a concentration range of 0.1 - 2% w/w BDE209. Relative standard deviation between triplicate determinations of BDE209 ranged from 0.32% to 0.42%. The limit of detection (LOD) obtained for BDE209 was 0.112 mg/kg, 4 orders of magnitude lower than the EU's maximum allowed concentration (MAC) in plastic. To our knowledge, this is the first method for compound specific quantification of BDE209 that does not require any sample preparation, reducing the analysis time from roughly 14 hours to 12 minutes with comparable quality of results.

Analytical Methods

Paper

Introduction

Brominated flame retardants (BFRs) are a class of chemicals used intentionally to impart flame retardancy in a wide range of consumer goods (such as electrical and electronic equipment (EEE), furniture, and textiles, etc.). They are also found in many more goods and materials as an unintentional result of poor recycling practices (kitchen utensils, children's toys, Food Contact Materials) [1,2]. One major class of BFR are the polybrominated diphenyl ethers (PBDEs). Of the several types of PBDE formulation manufactured and used, the deca-BDE mixture was dominant (83.3% of the global market demand) [3] which to some extent, can debrominate once released into the environment, resulting in a suite of less brominated congeners with enhanced toxicity and ability to bioaccumulate relative to the parent [3]. The RoHS recast Directive 2011/65/EU effective from 2013 sets limit values for polybrominated biphenyls (PBBs) and PBDEs (classes covering the most largely used additive BFRs, including deca-BDE) at a maximum level of 0.1 weight % in homogeneous materials. European standards give guidance on how to sample, prepare, extract and measure BFRs in plastics [4]. Recommended methods for monitoring compliance with RoHS limits for PBDEs can be divided into two main approaches: orientative screening and high-accuracy chemical analysis. Screening is preferred for in-situ evaluations as it is usually performed via solid sampling techniques like hand-held X-ray fluorescence spectroscopy (XRF) although this can only quantify Br as a proxy for the total BFR content, thereby running the risk of false positives. More conventional techniques are recommended for high-accuracy determination of BFRs like PBDEs. Specifically, RoHS requires GC-MS analysis to determine the BFR content in styrenic polymers (preceded by different sample preparation steps: sub-sample grinding, cryo-grinding, solvent extraction, extract filtration, selective precipitation for oligomer removal, and chromatographic purification). These traditional techniques can have a number of drawbacks aside from being time consuming and expensive. Soxhlet or pressurised liquid extraction of plastics often dissolves a substantial fraction of the matrix (polymer) together with the target compound, rendering the ensuing extract purification laborious and often leading to highly variable analyte recoveries. Furthermore PBDEs are present across a wide range of bromination level, from the lower brominated tri-BDEs and tetra-BDEs with a low boiling point to the most brominated (deca-BDE) with a very high boiling point. This makes it practically difficult to use the same GC-MS system set-up to analyze simultaneously in a single GC run:

Table 1 Composition of Reference Materials. Results obtained with Neutron Activation Analysis.

RM	BDE209 w/w %	BDE209 uncertainty ± %	Sb_2O_3 w/w %	TiO_2 w/w %	$CaCo_3$ w/w %
1	0	0	3	0.7	2.4
2	0.1	0.007	5	2.4	0
3	0.5	0.035	0	0.3	3
4	1	0.07	0.4	3	1.2
5	2	0.14	2.2	1.2	1.8

ideally two different GC columns are used, causing several analytical delays (run the samples on one system set-up first, then switch columns and run them again on the second set-up), although a better solution was achieved by Ballesteros-Gómez, [5] using GCxGC to resolve coeluting interferences in the second dimension, thus eliminating the need for two different GC runs. The high boiling point and its enhanced susceptibility to degradation and debromination when exposed at the elevated temperatures of the injector, column, ion source and detector make BDE209 a challenging analyte [6-16]. To face these analytical challenges novel methods for the quantification of BFRs have been developed recently combining GC, LC or GCxGC with a soft Ionization source (APCI) and a High Resolution time-of –flight mass spectrometer or for compound-specific screening using Direct Probe with HR-TOF [5].One attempt to develop a solid sampling, compound-specific analysis was made by exploring the potential of Direct Analysis in Real Time coupled with Time Of Flight Mass Spectrometry (DART-TOF-MS), [17] but results revealed it as constituting only a qualitative method to screen for the presence of BFRs in environmental matrices.

Against this backdrop, it is evident that a method that combines the convenience of a solid sampling technique with compound specific quantification is highly desirable.

We present here a simple, sensitive and rapid method using Direct Insertion Probe (DIP) in combination with Magnetic Sector High resolution Mass spectrometry (HRMS). This method characterizes target compounds without a chromatographic separation needed, solely via accurate mass determination combined with a traditional library search. To our knowledge, this is the first approach for compound-specific direct analysis of BFRs in polymers that does not require any sample preparation nor a GC or LC inlet. The method is validated via determination of BDE209 in

Acrylonitrile Butadiene Styrene (ABS) solid reference materials (RMs), but accurate mass determination can be applied to unambiguously identify other PBDE congeners.

Experimental

Overview

This method involves the use of matrix matched RMs for the compound specific quantification of BFRs in polymers. We used ABS as our polymeric matrix as it is one of the most common polymers used in Electrical and Electronic Equipment (EEE) and toys. Our target BFR was BDE209 as it displays a small temperature difference between evaporation and thermal degradation, as a proof of concept for the DIP method that samples the analytes via thermal desorption. Calibration of the method was carried out using RMs at 5 different concentrations of BDE209.

Reference materials

RMs loaded with different concentrations of deca-BDE were produced by Fachhochshule Muenster Labor für Instrumentelle Analytik (FMLIA). The method used to produce and test the RMs is described in detail elsewhere [18], but in summary, Br (in the form of deca-BDE) and Sb (in the form of Sb_2O_3) were added to an ABS terpolymer melt with the aid of an extruder. Sb_2O_3 is generally used as a synergist FR in combination with BFRs [19, 20]. A set of five different reference materials was produced in the form of pellets containing different mass fractions of both Br and Sb plus typical fillers commonly used in ABS (see Table 1) in order to best simulate the matrix of the samples.

Mass fractions of Br in the produced materials were determined (by FMLIA) via Neutron-Activation-Analysis (NAA). The uncertainty of NAA is about 7% (for exact values see Table 1). To assess macroscopic homogeneity a wavelength-dispersive X-ray spectrometer was used with RSD below 2% for Br. To assess microscopic homogeneity a synchrotron radiation μ-XRF (SR μ-XRF) was used. The spot size of the exciting beam was 200 μm, the RSD for Br was 0.7%.

Sampling

No sample preparation was required. A very small amount (≈0.045 mg) was scraped from the pellets of the RMs with a scalpel, accurately weighed with a precision scale (±0.0005 mg) and inserted in the aluminium crucibles for the DIP. The influence of the scale error on such a small sample is ±1.1%.

Instrumentation

The Thermo Scientific™ DFS™ Magnetic Sector High Resolution Mass Spectrometer (HRMS) was used for DIP-HRMS analysis. The probe temperature program is software controlled. The Thermo Scientific™ ISQ™ QD Single Quadrupole GC-MS System was used for the comparison of mass spectra obtained with the most common GC-MS technique (and relative sample preparation)[21].

The optimised conditions for BDE209 were obtained by varying one parameter at a time, performing a measurement and observing the influence of this variation on sensitivity, reproducibility and degree of fragmentation of the parent ion: faster DIP temperature ramps and higher electron energies were found to decrease the parent/daughter ratio and to increase the overall signal intensity, therefore a compromise between these two effects was found in the values reported in table 2:

Table 2 DIP-MS conditions

Ion Source temperature	260 ˚C
Source mode	EI Positive
DIP temperature programme	40(0.5˚C/min)-75-400 (2 min)
Scan mode	Magnetic scan
Mass range	30-1000 m/z
Resolution FWHM	20000
Electron energy	46 eV
Emission current	1 mA
Acceleration voltage	4800 V

To set the desired resolution of 20000 FWHM the reference gas (per fluoro kerosene (PFK), indicated in the mass spectrometric determination section) was monitored on mass 792.9499 m/z and the entrance and exit slits were closed recursively until the desired resolution was reached, these parameters were stored in the measurement conditions and the instrument response was regularly checked using the same reference gas.

Results and discussion

Mass spectrometric determination

As no GC column is used, the only time difference in vaporisation is dictated by the compound's vapour pressure. The RMs we used to test this method were loaded with BDE209, although due to the process they underwent to be produced (melted and extruded several times to ensure homogeneity), some thermal decomposition is likely to have produced a small amount of decomposition products inside the polymer (Fig. 1).

Thermo Scientific™ Mass Frontier Software was used to simulate all the potential BDE209 fragments and hence identify target ions, for this method we chose the molecular ion of decaBDE (m/z 959) and its main breakdown product (m/z 799) octaBDE.

Isotopic patterns and exact masses corresponding to these two ions were simulated using the Thermo Scientific™ Xcalibur™ Software. The exact masses were used to calculate the mass measurement error (ppm) following the expression (1):

$$\Delta\square_{\square} = \frac{(\square_{\square} - \square_{\square})}{\square_{\square}} \times 10^{6} \qquad (1)$$

Where m_m is the measured accurate mass and m_c is the exact mass. The deviation of the measured masses from the exact masses was for all isotopologues of BDE209 (averaged over 20 scans) less than 1 ppm using a dedicated pre calibrated method based on Reference material PFK which uses all the exact masses contained in the PFK mixture to perform a polynomial correction of the measured accurate masses (see Fig. 2 and Table 3).

Table 3. Mass Table of measured isotopes

m/z	Relative intensity	Delta (ppm)	Composition
951.1749	4.34	**-0.88**	C_{12} O Br_9 [81]Br
953.1735	19.34	**-0.16**	C_{12} O Br_8 [81]Br_2
954.1772	2.5	**0.24**	C_{11} [13]C O Br_8 [81]Br_2
955.1718	51.57	**0.16**	C_{12} O Br_7 [81]Br_3
956.1756	6.25	**-0.41**	C_{12} [13]C Br_5 [81]Br_5
957.1696	86.22	**-0.01**	C_{12} O Br_6 [81]Br_4
958.1725	10.78	**-0.46**	C_{11} [13]C O Br_6 [81]Br_4
959.1677	100	**0.16**	C_{12} O Br_5 [81]Br_5
960.1711	12.92	**0.22**	C_{11} [13]C O Br_5 [81]Br_5
961.1658	81.39	**0.38**	C_{12} O Br_4 [81]Br_6
962.1689	10.16	**0.07**	C_{11} [13]C O Br_4 [81]Br_6
963.1634	45	**0.00**	C_{12} O Br_3 [81]Br_7
964.1666	5.79	**-0.13**	C_{11} [13]C O Br_3 [81]Br_7
965.1613	16.71	**-0.05**	C_{12} O Br_2 [81]Br_8
964.1646	1.76	**-0.16**	C_{11} [13]C O Br_2 [81]Br_8
967.1596	3.52	**0.33**	C_{12} O Br [81]Br_9

Verification of the DIP-HRMS method

Octa-BDE and deca-BDE were measured and their ratio evaluated to test the reproducibility of the fragmentation.

Although selected ion mode analysis can provide better sensitivity and transient signals that are easier to interpret, we decided to acquire in the complete mass range (m/z 30-1000) for BDE209 for three reasons: (a) when BDE209 is present in consumer goods, whether it is added voluntarily or not, its concentration is usually orders of magnitude higher than the detection limits of the DFS Magnetic Sector GC-HRMS; moreover the regulatory limits set a relatively high concentration threshold 0.1% in homogeneous material; (b) for quantitative purposes it is very important to include in the calculation every fragment (including molecular Br) deriving from the parent ions present in the samples. This approach allowed us to understand whether it was reasonable to assume that - granted a very stable fragmentation yield - the total Br would have been linearly proportional to any of the main fragments produced (octa-BDE and nona-BDE); and (c) such a wide mass range - covering the vast majority of commonly used BFRs - delivers the flexibility to identify and quantitate different compounds simultaneously.

The calibration curve was determined by analyzing each of the five solid RMs (0 %, 0.1 %, 0.5 %, 1 %, 2% w/w of BDE209) in triplicate. Intensities were considered selecting the 3 most intense m/z values from the isotopic pattern and averaging the intensities of the time signals corresponding to those 3 masses. Scans from the tails of the transient signal were excluded when their relative intensity was less than 5% of the most intense scan (this corresponds to ca. 40 scans for each "peak").

The signal intensity of BDE209 (average intensity between m/z 959, 957, 961) was plotted against the reference value of the RMs. In the same way, the signal intensity of the -2Br fragment (average intensity between m/z 799, 797, 801) was plotted against the reference value. The correlation factor R^2 was >0.999 for both BDE209 and his octabrominated breakdown product, showing linearity over the selected range. The calibration curve for BDE209 was obtained by averaging the signal intensity of the three most abundant isotopologues of BDE209, m/z 959, 957, 961 for each calibration level (Fig. 3a). The calibration curve for the main fragmentation product of BDE209 -which is octaBDE- was obtained by averaging the signal intensity of the three most abundant isotopologues of octaBDE, m/z 799, 797, 801 for each calibration level (Fig. 3b).

The LOD was defined as in the ICH1 Guidance (Q2,R1: Validation of Analytical Procedures) as:

$$\square\square\square = 3.3\sigma/S$$

where σ = the standard deviation of the response on the triplicate measurement of blank samples (RM BDE209) and S = the slope of the calibration curve. The noise – defined as the

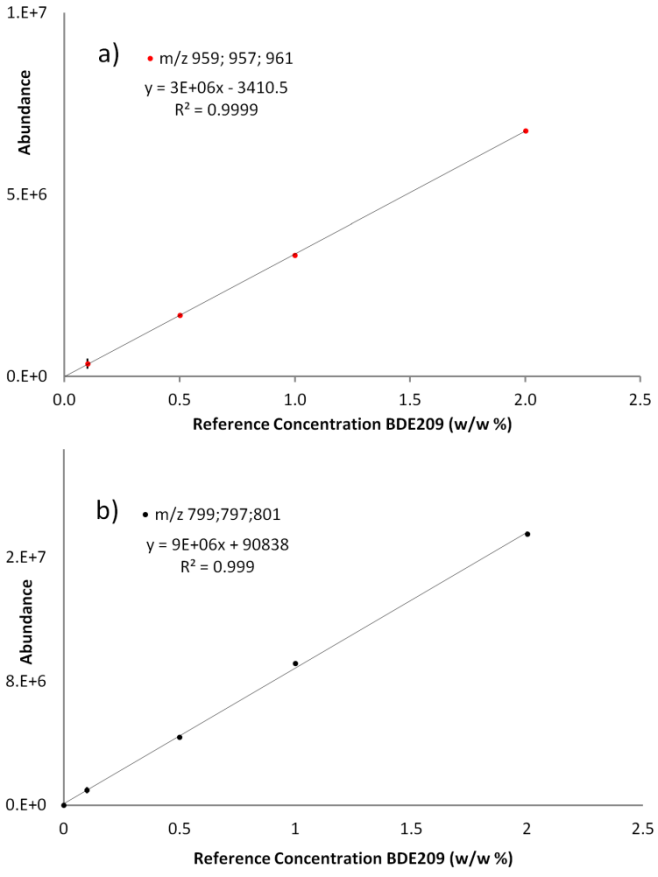

Fig. 3 Calibration curves and linearity for the analysis of (a) [BDE209]+, (b) [BDE209-Br2]+ obtained by DIP. Error bars are the SD between triplicate measurements of each RM

intensity of the signal given by the target mass on a blank measurement- was below 1/3 of the instrument detection limits. This result was foreseeable, considering that each sample, and the crucible containing it, was removed from the probe before inserting a new sealed crucible containing a different sample, therefore no physical residues of the previous sample could be left on the one following (unlike a traditional GC analysis, where polymeric residues might build up in the injector liner and in the column and create a memory effect). The calculated LOD with this method was 0.112 mg/kg, the LOQ was 1.120 mg/kg for BDE209, slightly lower than a similar study performed with Direct Exposure Probe (DEP) [22], and with the advantage of no sample preparation needed.

The memory effect was evaluated by calculating the RSD% between triplicate measurements of the most concentrated RMs: the percent variation was 0.47% and no increasing trend was observed.

Intraday stability was evaluated by performing control runs of RM3 at the beginning, in the middle and at the end of each day of analysis. Over 3 days the intraday RSD of the signal intensity for BDE209 averaged at 1.96%, while interday RSD was 0.51%.

The method was applied to 21 real polymeric samples (children's toys and food contact articles, Table 1, SI) for which the BDE209 concentration was measured. BDE209 data and total elemental Br measured with an X-Ray Fluorescence spectrometer were plotted to evaluate if a correlation existed between the two metrics. BDE209 was detected in a concentration ranging from 8.8 mg/kg to 4327 mg/kg. Considering that these data refer to real samples, containing a suite of different BFRs, each potentially contributing to the total elemental Br concentration; the correlation (R^2=0.86) between our BDE209 concentration measurements and those for total Br is striking. Moreover, our measurements of BDE209 -which is likely to be a fraction of the total BFR content- never exceeded those of total detected Br (Fig.1, SI).

Reproducibility of the fragmentation ratios

The ionisation behaviour was tested for reproducibility by selecting m/z 799 and m/z 959 from the time signal and measuring the intensity for these masses over the selected time interval. DIP offers a specific advantage with respect to GC-MS analysis: as there is no column or injector between the sample induction system and the ionization volume, it is possible to differentiate between breakdown products (caused by thermal degradation) and ionization fragments (produced by the EI ionization process). This is easily done by comparing the time signals for the molecular ion and for its possible moieties as shown in Fig.1: a) and b) show the overlap in intensities of the time signal respectively for the decabrominated ion and the octabrominated ion, meaning that the latter was formed simultaneously in the source, as a fragment of the former. Following this approch we are also able to say that as the pentabromophenate ion (d)) was detected at the same time of molecular bromine (g)), the debromination happened in the ion source and not as a thermal process in the sample; moreover, time signals d) and g) are both detected before the deca- and octa brominated fragments meaning that their parent ion was already present in the reference material before the insertion in the source.

The ratio between the molecular ion and its main fragmentation product was – for all measured concentrations - 3.1±0.04 (see table 4), showing it to be independent of the sample concentration and suggesting very reproducible fractionation behaviour. This is important as it allows subtraction of the contribution made by the BDE209-2Br fragment to the signal for m/z 799, thereby facilitating quantification of any octa-BDEs present.

A comparison between the mass spectrum of the sample RM obtained using our DIP-HRMS method and that obtained via GC-MS following traditional sample preparation methods and liquid sampling in Fig. 4 shows how the ratio between m/z 799 and m/z 959 is almost two times higher for the traditional GC-MS technique. The thermal decomposition is reduced in the DIP method because the sample is introduced in a chamber under vacuum (instead of under pressure as it would be in a GC injector) therefore the sufficient vapor pressure is reached at lower temperatures.

Table 4. Fragmentation ratio between the two main BDE209 ions.

Reference BDE209 w/w %	Ratio m/z 799 and m/z959	SD
0.1	3.002	0.04
0.5	3.079	
1	3.051	
2	3.002	

Conclusions

The method reported here represents a rapid, accurate way of performing compound specific quantification of BDE209 in polymers, that avoids completely the labour intensive, time consuming preparation of the samples.

Because of the conveniently small sample size required for our analysis (~0.045 mg), this virtually non-destructive method is designed to be used on articles still in use as domestic appliances (therefore allowing application in studies requiring identification of putative source items in human exposure studies) as well as future waste items. With a linear range covering a concentration span of 19,000 mg/kg which for new and recycled plastics represents the full range of detected concentrations (a considerable improvement with respect to a recent DEP study [22], where the calibration span was from 0.5 to 16 mg/kg) this technique can be a valid, easier, alternative to existing analytical methods for monitoring RoHS compliance in consumer goods. These articles belong now to a second and

third generation of recycling; and thus generally contain lower concentrations of BFRs (compared to the concentrations of the intentionally added BFRs in older items) as the contaminated polymeric fractions have been mixed with new polymers [4][23].

This is illustrated by a recent study where a Direct Injection Probe coupled with a HR-TOF-MS was used to screen BFRs in plastics, in which the concentration of FRs in the analyzed samples never exceeded 1.6% in WEEE items [5].

Our method is tested here for BDE209 in ABS as a proof of concept, but given suitable solid RMs, quantification of lower brominated compounds in other polymers and over wider calibration ranges will be feasible. DIP-MS optimised for PBDEs in plastics is able to give results that are as accurate as GC-MS [24] but are at least 50 times faster to achieve. Considering the burgeoning need for quantification of BFRs in waste samples [IEC 62321], we believe our method will be of significant value.

Future developments

This solid sampling technique has the advantage of being completely solvent-free and hence a "greener" alternative to techniques that involve sample preparation. It would be desirable – in order to make it routinely available – to have a more complete set of solid reference materials that represent the 3 most widely used FRs (pentaBDE, octaBDE and decaBDE commercial mixtures) in their respectively most commonly-used polymers (mainly ABS, PS, and PP/PE). The resources required for production of such suitable reference materials for matrix-matched calibrations with this method would be significantly less than the multitude of sample preparations this technique would render redundant.

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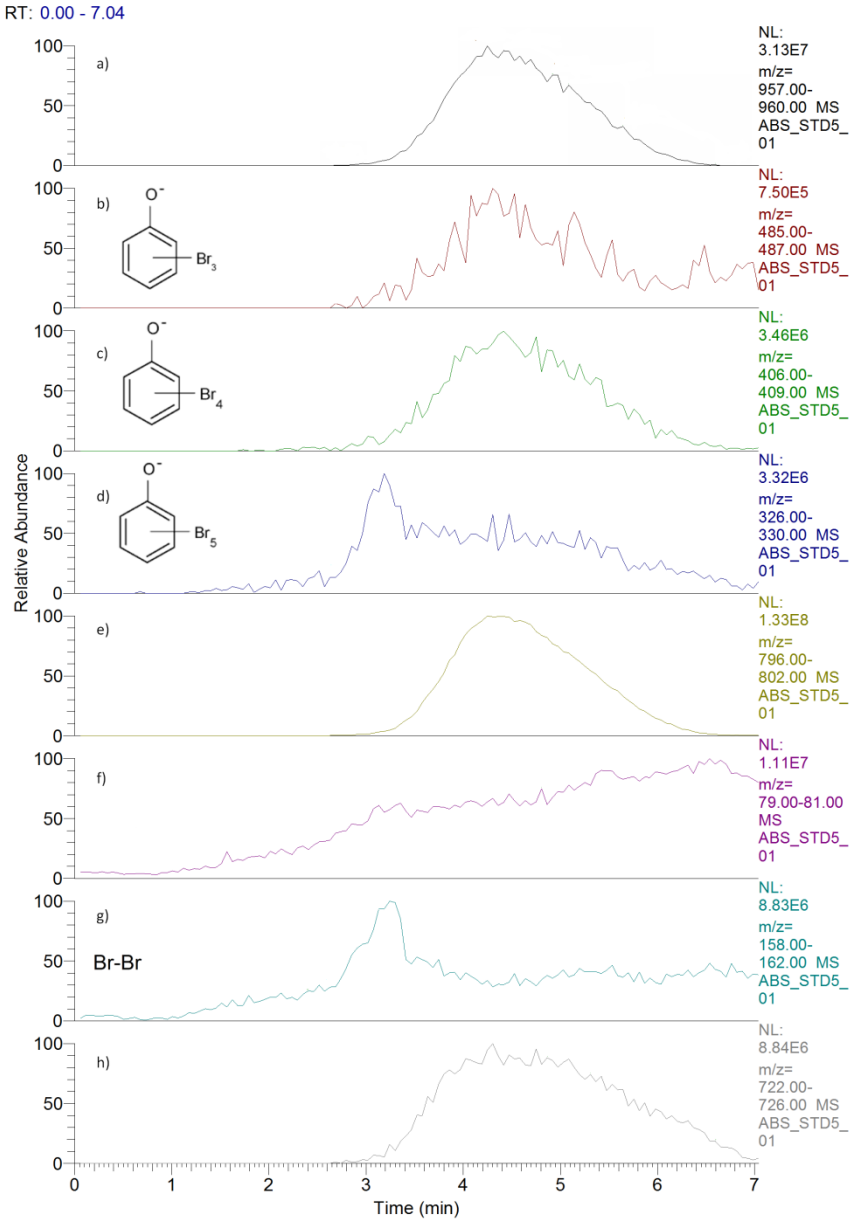

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Fig. 1. Time signal obtained with DIP-HRMS (selected over the entire time signal for a) m/z 957-960; b) m/z 485-487; c)m/z 406-409; d) m/z 326-330; e) 796-802; f) m/z 79-81; g) m/z 158-162; h) m/z 722-726. It is possible to notice that the formation of the penta brominated ions (d)) corresponds to a simultaneous release of Br_2 molecules (g)).

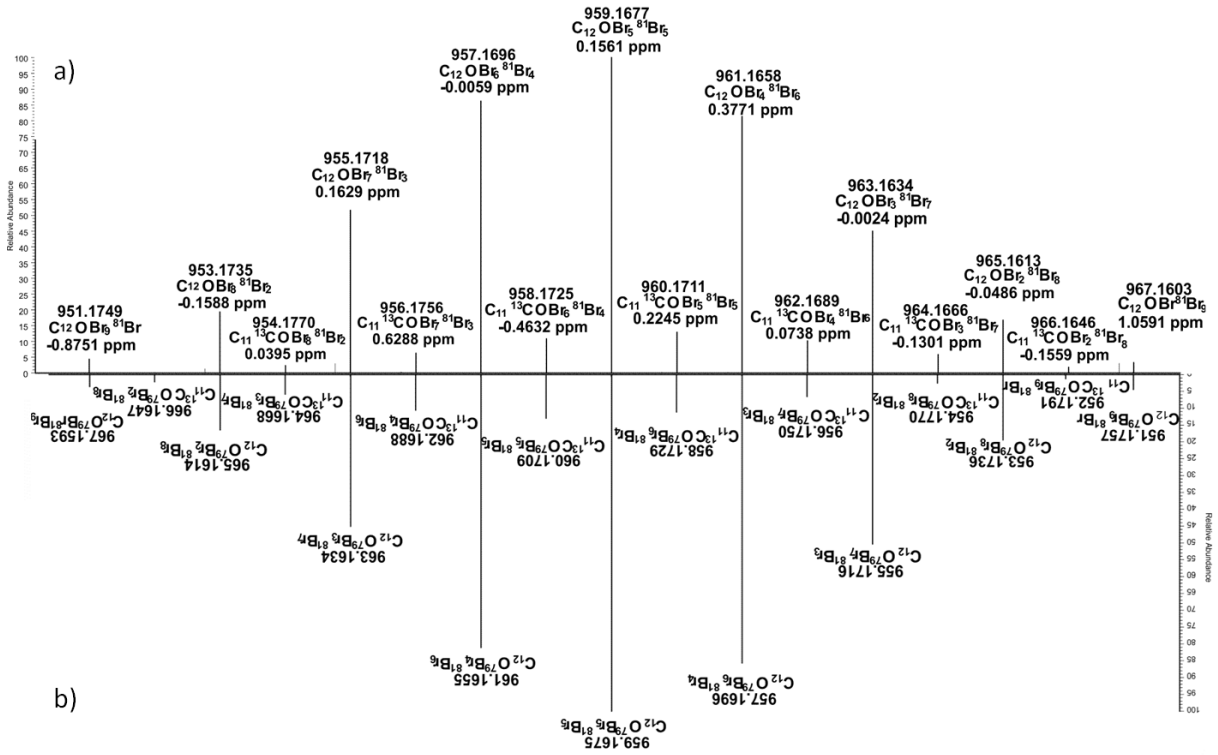

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Fig. 2. Comparison of a) accurate masses measured over 20 scans for BDE209 (reported in table 3), and b) their calculated exact value.

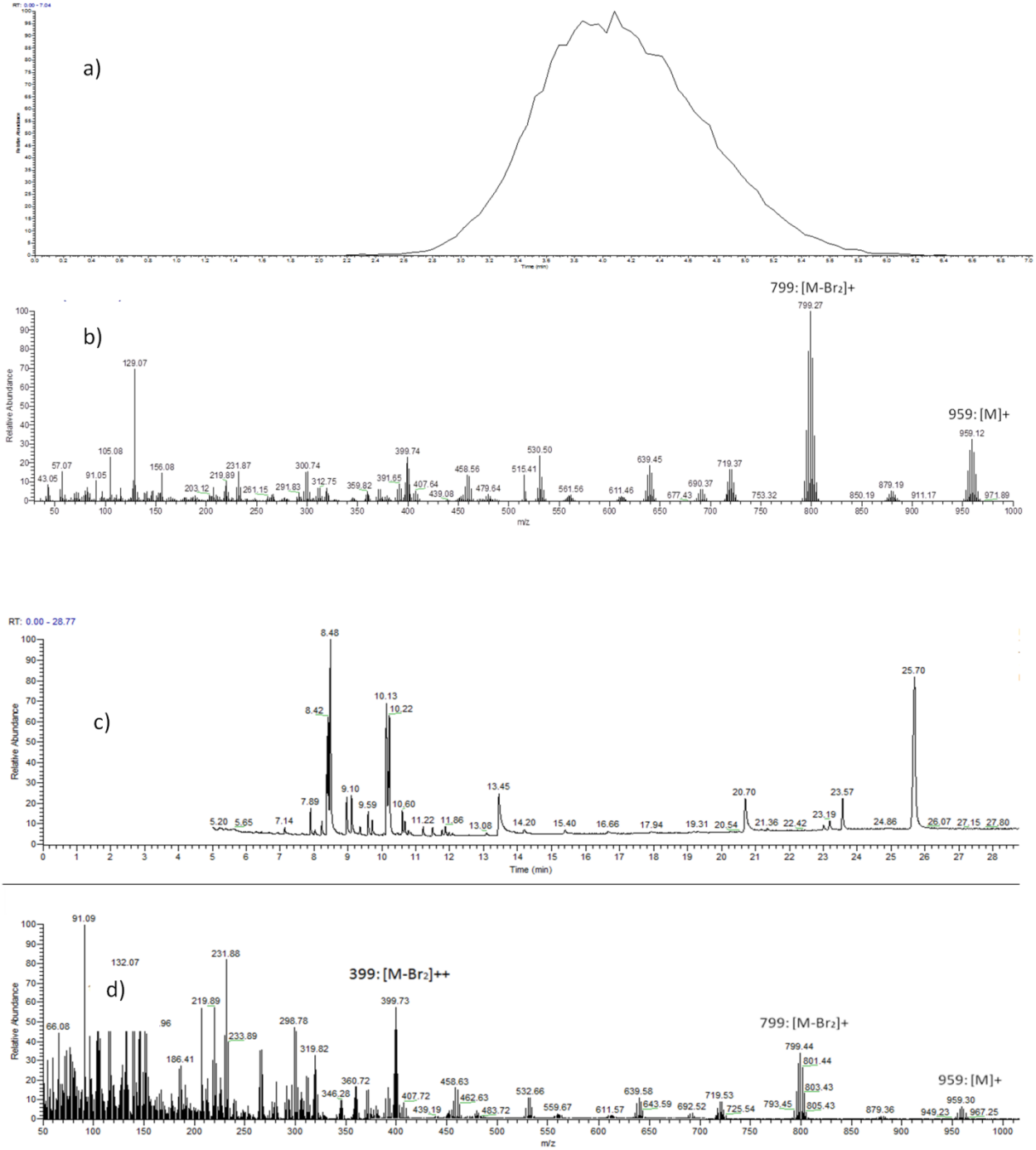

Fig. 4 TIC for the same RM (ABS with 0.5% BDE209) obtained with a)DIP-HRMS and)GC-MS. Mass spectra obtained with b) DIP-HRMS (selected over the entire time signal for m/z 799; 959), and d)GC-MS (selected over the chromatographic peak RT:25.70 corresponding to BDE209)